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Effect of Free Air Carbon dioxide Enrichment (FACE) on the chemical composition and nutritive value of wheat grain and straw

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ABSTRACT

The global impact of an increased concentration of CO_2 in the atmosphere on plants has been studied extensively, but little information has been published on the effect of enrichment of atmospheric CO_2 on the nutritive value of grain and straw used as ruminant feeds. This paper reports the chemical composition and nutritive value of grain and straw harvested from the drought tolerant hard red spring wheat (*Triticum aestivum* L.) variety Yecora Rojo managed with two carbon dioxide regimes (ambient, 350 μl/l and elevated, 550 μl/l), two rates of nitrogen application (low N: 53 kg N/ha and high N: 393 kg N/ha) grown under a water-fed (*i.e.*, no deficit) regime. Accumulation of carbon in straw did not differ among crops grown under elevated CO_2 and low N supplementation and crops grown under ambient CO_2 with low levels of N supplementation. Increased N application increased sequestration of C ($P<0.05$) compared to straw from crops grown under ambient CO_2 concentration. Low levels

Abbreviations: ADF_{om}, acid detergent fibre; CP, crude protein; DM, oven dry matter; FACE, Free Air Carbon dioxide Enrichment; NDCD, neutral detergent cellulase digestibility; $aNDF_{om}$, neutral detergent fibre; WSC, water soluble carbohydrate.

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of N application and elevated CO_2 led to straw containing similar concentrations of N to those grown under ambient CO_2 conditions. Increasing N application to crops grown under ambient concentrations of CO_2 elevated the concentration of N ($P<0.01$) whereas crops at elevated concentrations of CO_2 did not accumulate N to the same extent. Differences in the non-structural carbohydrate and cell wall content reflected the patterns for total C. No effect of increasing the concentration of CO_2 on WSC, $aNDF_{om}$, ADF_{om}, hemicellulose, cellulose and lignin (sa) occurred. There was a small decline (−26 g/kg; $P<0.05$) in the concentration of $aNDF_{om}$ in straw from crops that had received high N input. The ratio of lignin to total N was higher in straw harvested from plots with elevated CO_2 (33.5:1) compared with ambient CO_2 (24.6:1). No changes in the total C content occurred for grain samples in response to CO_2 concentration or supplemental N fertiliser. No interaction between supply of N and CO_2 concentration occurred. Changes in the total N content of grain in response to treatments were similar to the changes observed in the straw fraction. The increases in concentration of N incorporated into grain were higher from crops grown under enriched concentrations of CO_2 (*i.e.*, +8.6 g/kg; $P<0.01$) than for crops grown under ambient supply of CO_2 (+3.5 g/kg; $P<0.05$). Differences in concentration of starch in the grain with increasing supply of N from fertiliser occurred under FACE conditions ($P<0.05$), but not for grain harvested from those grown under ambient CO_2 levels. No effect of changing concentrations of CO_2 were observed for ADF_{om}, lignin (sa), cellulose and neutral detergent cellulose digestibility but concentrations of $aNDF_{om}$ ($P<0.05$) and hemicellulose ($P<0.05$) were higher in grain grown under ambient concentrations of CO_2 irrespective of supply of N to the crop. Although effects of elevated concentrations of CO_2 on grain and straw quality were expected, this poses concerns for livestock production in systems that use lower levels of agronomic inputs. Elevated concentrations of CO_2 in the ambient environment were beneficial for development of above ground biomass and grain yield as measured by thousand-grain weight. However, straw and grain quality, in terms of crude protein and the crude protein to energy ratio will be affected by increasing concentrations of CO_2 in the atmosphere, and this may lead to a reduction in the total supply of crude protein in crops used by livestock.

1. Introduction

The global impact of the increased concentration of CO_2 in the atmosphere on plants has been the subject of intense study in recent years (Hocking and Meyer, 1991; Baxter et al., 1994; Akin et al., 1995a,b; Hirschel et al., 1997; Fangmeier et al., 1999; Sinclair et al., 2000; Pinter et al., 2000; Manderscheid et al., 2003; Asseng et al., 2004). Despite their importance to the world food supply, little information has been published on effects of higher atmospheric CO_2 on plant constituents and nutritive value of grain and straw. The annual global consumption of wheat grain is in excess of 550 million tonnes (FAO, 2002) of which approximately two-thirds is used for human consumption and one-sixth is fed to ruminants and non-ruminants. The remainder is used as seed for industrial use (*e.g.*, manufacture of starch) or lost post-harvest (Fowler, 1999). Straw and cereal crop residues are especially important in developing countries, where agronomic inputs and water supply can be restricted and crop residues are a main component of the diets of ruminants (Preston and Leng, 1987; Ørskov, 1991). Straw also is used for the production of industrial products (*e.g.*, paper, construction materials, feedstock chemicals) in some parts of the world.

Atmospheric CO_2 enrichment enhances the rate of growth, but not necessarily the development, of C_3 and C_4 agricultural crops, even under conditions of limited nutrient supply or water availability (Akin et al., 1995a,b; Pinter et al., 2000; Idso and Idso, 2001; Manderscheid et al., 2003; Asseng et al., 2004). Therefore, enrichment increases the biomass above ground and yield of total biomass could be enhanced by 30% if the concentration of CO_2 in the atmosphere were increased to 600 μl/l from ambient (approximately 370 μl/l) concentrations (Kimball, 1983). However, this enhancement in yield is not consistent with declines in transpiration, or increases in leaf area index. Many of the recent studies (*e.g.* ESPACE programme, see for instance Mitchell et al., 1999; FACE see Pinter et al., 2000; Lanzhou University, China, see Wu et al., 2004) have focussed on the impact of elevated CO_2 on plant N balance and C supply to secondary plant compound synthesis. However, little data exists on potential changes in chemical composition of cereal grain and, more especially, straw for livestock production and feed processing.

This paper reports the chemical composition and nutritive value of grain and straw harvested from the drought tolerant hard red spring wheat (*Triticum aestivum* L.) variety Yecora Rojo managed under two CO_2 regimes with two rates of N application under a water-fed (*i.e.*, no deficit) regime, and discusses the implications of changes in nutritive value from elevated concentrations of CO_2.

2. Materials and method

The experiments were conducted in 1996 and 1997 at the Free Air Carbon dioxide Enrichment (FACE) facility established at the Maricopa Agricultural Center, 40 km south of Phoenix, AZ, USA.

2.1. FACE experiment

The FACE technique was used to enrich air with CO_2 in circular plots within a standing crop of wheat (Wall and Kimball, 1993; Pinter et al., 2000). Four replicate arrays (25 m diameter toroidal plenum ring) were positioned on the soil surface after the crop was sown and the air was enriched with CO_2 by blowing CO_2 enriched air of variable CO_2 content at a rate of 40 m^3 air/min into the plenum, and releasing the enriched air via 32 vertical tri-directional jets near to the top of the crop canopy.

The amount of CO_2 released into each FACE array was maintained by feedback from monitoring CO_2 concentration, wind speed and direction at the centre of each ring. The flow of CO_2 was updated every second and the choice of exit vent was controlled every 4 s. This process was validated by Nagy et al. (1994) who reported that minute by minute concentrations of CO_2 at the centre of the array varied no more than 10% of target concentration 90% of the time. A target concentration of 550 μl/l was achieved in the enriched treatment throughout the growing season. Air blowers were installed in the non-CO_2 enriched arrays (*i.e.*, ambient) to ensure no indirect microclimatic changes confounded the effect of treatments.

2.2. Site characteristics, crop establishment and management

A seed bed was prepared in Trix clay loam [(fine-loamy, mixed calcareous hyperthermic Typic Torrifluvents (FAO: Fluvisol)] in December 1996. The top 0.7 m of the soil profile was homogenous with a soil textural characterisation of 300 g/kg sand, 310 g/kg silt, 340 g/kg clay and 50 g/kg organic matter. The profile below 0.7 m the soil was predominantly sand. The estimated plant available water content (as determined by volumetric soil water content) in the root zone (effective depth of 1.3 m) was 130 mm and irrigation was triggered when 30% depletion occurred in an array. Irrigation of each array was achieved using sub-surface seep irrigation with water supplied to replenish any deficit and maintain the volumetric water content in the root zone at 130 mm.

The hard red, drought tolerant spring wheat variety Yecora Rojo was sown at a rate of 109 kg/ha on 15 December 1996. The crop was drilled into the prepared seed bed in rows spaced 0.25 m apart, and the irrigation system was installed at a depth of 0.2 m in the soil between alternate rows. The crop was irrigated using a field sprinkler system until 28 December 1996 during crop establishment. Thereafter sub-surface irrigation was applied until crop harvest (Fox et al., 1992; Hunsaker et al., 1996). The FACE arrays were installed on 28 December 1996 and enrichment of CO_2 commenced on 3 January 1997. The plant establishment in early January 1997 was 194 plants/m^2. Final harvest of grain and straw occurred on 29 and 30 May 1997.

The N fertiliser regimes applied in the split plot design were nominally 75 kg N/ha (low N regime) and 350 kg N/ha (high N regime). However, the supply of N to the low and high N regimes varied reflecting the findings of previous studies at the site, concentrations of N in the soil at crop establishment, and N in irrigation water applied throughout the growing season (Sinclair et al., 2000). The application of ammonium nitrate was split into three (low N regime) or four applications (high N regime) through the irrigation system. The low N regime received N on 30 January 1997 (5 kg N/ha), 5 March 1997 (5 kg N/ha) and 18 March 1997 (5 kg N/ha). The treatment also received 38 kg N/ha in the irrigation water and the average pre-establishment concentration of N was 69 kg N/ha. The low N regime received supplemental N at a rate of 53 kg N/ha and the high N regime received supplemental N on 30 January 1997 (50 kg N/ha), 5 March 1997 (125 kg N/ha), 18 March 1997 (125 kg N/ha) and 50 kg N/ha on 22 April 1997. The high N regime also received 43 kg N/ha via irrigation water and had a pre-establishment N concentration of 145 kg N/ha. The high N regime therefore received 393 kg N/ha during the 1997 growing season.

2.3. Measurements

At crop maturity, whole wheat plants (30 plants per array) were cut at ground level, air-dried at 60 °C and stored for subsequent chemical analysis. The plants were dissected into straw (*i.e*., including leaf fraction) and grain (*i.e*., threshed, discarding the chaff). The straw and grain fractions were analysed for total C and N using a CHNOS elemental analyser (PerkinElmer Series II CHNOS Analyser 2400, Waltham, MA, USA). The fractions were analysed by sequential extraction for neutral detergent fibre ($aNDF_{om}$), acid detergent fibre (ADF_{om}) and lignin (solubilisation of cellulose with sulphuric acid; lignin (sa)) according to Van Soest et al. (1991) and Udén et al. (2005). The total ash of the residues was measured after incineration of the sample at 550 °C for 6 h. Hemicellulose was calculated as the difference between $aNDF_{om}$ and ADF_{om} by sequential extraction and cellulose as acid detergent lignin free ADF. Neutral detergent cellulose digestibility (NDCD) was assessed according to Dowman and Collins (1982) with a pre-incubation of grain samples with thermo-stable α-amylase. All data for $aNDF_{om}$, ADF_{om}, lignin (sa), hemicellulose, cellulose and NDCD are reported on an ash free basis. Water soluble carbohydrate, total ash and crude protein (CP) were determined according to MAFF (1986). Grain protein content was determined by near infra-red spectroscopy (QN1000 NIR analyser, Leco Instruments Ltd., Stockport, Cheshire, UK) after samples were milled to a nominal particle size of 500 μm. The gross energy of the samples was calculated by complete combustion of the sample in oxygen by adiabatic bomb calorimetry (Gallenkampf autobomb, Gallenkampf, Loughborough, UK). Starch content of the grain samples was measured by polariography after conversion to glucose using α amylase according to AOAC method 29.022 (1965).

2.4. Statistical analysis

The experiment was a split plot design and was analysed for main effects of concentration of CO_2 (ambient *versus* elevated; 1 d.f.) and level of N fertiliser (low *versus* high; 1 d.f.) and an interaction of CO_2 and N (1 d.f.) using analysis of variance (ANOVA). Data that are reported in the dry matter (DM) and ratio data were transformed prior to ANOVA using the arcsin procedure (Mead et al., 1993). *Post hoc* analysis of data to identify mean differences between main effects was conducted according the method of Tukey (Mead et al., 1993). All statistical analysis was performed using GENSTAT version 8.2 (Lawes Agricultural Trust, 2006).

3. Results

3.1. Chemical composition of the straw fraction

No effects of elevated concentrations of CO_2 on total C content of straw occurred in any treatment (Table 1). The consequence of elevated CO_2 on total N content of straw differed from that for total C in

Table 1
Chemical composition of straw harvested from FACE and ambient CO_2 plots receiving low or high levels of N supplementation

	N level				s.e.d	Treatment effects		
	Low (53 kg N/ha)		High (393 kg N/ha)			[CO_2]	[N]	[CO_2] × [N]
	Ambient [CO_2]	FACE	Ambient [CO_2]	FACE				
Total C (g/kg DM)	409	402	412	409	5.44	ns	ns	ns
Total N (g/kg DM)	2.4	1.7	5.2	4.6	1.71	ns	P<0.05 (amb) P<0.001 (FACE)	ns
C:N	170	236	79	89	41.4	ns	P<0.05 (amb) P<0.05 (FACE)	ns
Water soluble carbohydrate (g/kg DM)	16.0	19.6	19.0	18.7	2.72	ns	ns	ns
aNDF$_{om}$ (g/kg DM)	811	816	785	804	8.68	ns	ns (amb) P<0.05 (FACE)	ns
ADF$_{om}$ (g/kg DM)	558	547	542	537	8.44	ns	ns	ns
Lignin (sa) (g/kg DM)	59	57	48	46	5.73	ns	ns	ns
Hemicellulose (g/kg DM)	253	269	243	267	7.22	ns	ns	ns
Lignin (sa):N	24.6	33.5	9.2	10.0	4.22	ns ns	P<0.01 (amb) P<0.05 (FACE)	ns
Ash (g/kg DM)	68	66	62	68	5.42	ns	ns	ns
Neutral detergent cellulase digestion (g/kg DM)	387	395	394	401	11.27	ns	ns	ns

L = low level of N supplementation (53 kg N/ha); H = high level of N supplementation (393 kg N/ha). ns = not significant (*i.e.*, P>0.05); amb = ambient CO_2 concentration.

that at low levels of supplemental N fertiliser, there was a slight reduction (*i.e.*, 0.7 g/kg DM; P>0.05) of total N incorporated into straw harvested from the FACE treatment. As expected, the straw harvested from the crops grown under ambient concentrations of CO_2 but receiving a high level of N fertiliser had substantially higher concentrations of N (P<0.01) than straw harvested from the crop receiving a low level of N. These differences were accentuated in crops harvested from the FACE treatments, with an increase in concentration of 2.9 g/kg DM (P<0.001) in straw harvested from plots that had received high levels of nitrogen fertiliser *versus* 2.8 g/kg DM with an ambient CO_2 concentration. There was no interaction between level of N and CO_2. The effect of elevated CO_2 on the C:N ratio of crops receiving low levels of N fertiliser was a "dilution" of N in relation to the incorporation of C. Hence, the ratio increased from 170:1 to 236:1. However if the crop received a high level of supplemental N, the difference in "dilution" of N between crops grown under conditions of elevated concentration of CO_2 and those grown in ambient CO_2 was reduced (79:1 for low N, ambient CO_2 *versus* 89:1 for high N, enriched CO_2).

Differences in non-structural (WSC) and structural carbohydrate (aNDF$_{om}$, ADF$_{om}$ and lignin (sa)) reflected the differences in the total C content of the straw. No effects of increasing the concentration of CO_2 on WSC, aNDF$_{om}$, ADF$_{om}$, hemicellulose, cellulose and lignin (sa) occurred. There was a small decline (*i.e.*, −26 g/kg; P<0.05) in the concentration of aNDF$_{om}$ in straw samples collected from plots that had received high levels of N fertiliser. The ratio of lignin (sa) to total N increased in straw harvested from FACE plots (*i.e.*, 24.6:1 with ambient CO_2 *versus* 33.5:1 FACE). The observations parallel patterns observed for C:N ratio between different CO_2 treatments with differences between the ratio (lignin (sa):N *versus* C:N) being almost identical. The situation differed for the comparison between the C:N ratio and lignin (sa):N when wheat crops had received a high level of supplemental N, and differences between elevated CO_2 and ambient lignin (sa):N ratios were substantially lower than the C:N ratio. No differences in total ash or neutral detergent cellulose digestibility occurred between CO_2 treatments or level of N fertiliser (Table 1).

3.2. *Chemical composition of grain*

No changes in the total C content occurred for grain samples in response to CO_2 concentration or supplemental nitrogen fertilizer (Table 2). Furthermore, no interaction occurred between the supply

Table 2
Chemical composition, nutritive value and thousand grain weight of wheat harvested from FACE and ambient CO_2 plots receiving low or high levels of N supplementation

	N level				s.e.d	Treatment effects		
	Low (53 kg N/ha)		High (393 kg N/ha)			$[CO_2]$	[N]	$[CO_2] \times [N]$
	Ambient $[CO_2]$	FACE	Ambient $[CO_2]$	FACE				
Total C (g/kg DM)	437	436	443	449	12.66	ns	ns	ns
Total N (g/kg DM)	19.6	21.9	25.2	30.9	3.57	P<0.01	P<0.05 (amb) P<0.01 (FACE)	P<0.01
C:N	22.2	19.9	17.5	14.4	2.15	ns	ns (amb) P<0.01 (FACE)	ns
Water soluble carbohydrate (g/kg DM)	54	58	46	53	3.61	ns	ns	ns
$aNDF_{om}$ (g/kg DM)	147	114	136	122	9.45	P<0.05	ns	P<0.05
ADF_{om} (g/kg DM)	27	25	22	23	4.49	ns	ns	ns
Lignin (sa) (g/kg DM)	7.2	6.8	5.9	5.2	1.82	ns	P<0.01 (amb) P<0.05 (FACE)	ns
Hemicellulose (g/kg DM)	120	89	114	99	7.55	ns	ns	ns
Lignin (sa):N	0.37	0.31	0.23	0.17	0.15	ns	ns	ns
Ash (g/kg DM)	17	16	19	18	2.22	ns	ns	ns
Starch (g/kg DM)	522	564	537	577	8.77	P<0.01	ns (amb) P<0.05 (FACE)	ns
Crude protein (g/kg DM)	116	85	138	139	6.75	P<0.01	P<0.05 (amb) P<0.01 (FACE)	P<0.01
Gross energy (MJ/kg DM)	18.6	18.8	18.7	18.9	0.04	P<0.001	P<0.05 (amb) P<0.01 (FACE)	ns
Neutral detergent cellulase digestion (g/kg DM)	848	856	851	849	5.17	ns	ns	ns
Grain weight (g/1000 grains)	51.3	53.6	53.7	51.0	3.22	ns	ns	ns

L = low level of N supplementation (53 kg N/ha); H = high level of N supplementation (393 kg N/ha). ns = not significant (*i.e.*, P>0.05); amb = ambient CO_2 concentration.

of N and CO_2 concentration. The changes in the total N content of grain in response to the various treatments were similar to the changes observed in the straw fraction. Increasing the concentration of CO_2 in the air when the crop did not receive high levels of supplemental N fertiliser decreased (P<0.01) N content of the grain. However, the level of N incorporated in the wheat crops grown under elevated concentrations of CO_2, with high levels of N supplied from fertiliser, were similar to those for crops grown under ambient CO_2 conditions. The increases in concentration of N of the grain due to fertilisation were higher from crops grown under enriched concentrations of CO_2 (*i.e.*, +9.0 g/kg; P<0.01) than for crops grown under ambient supply of CO_2 (*i.e.*, +5.6 g/kg; P<0.05). A similar pattern occurred for the CP content of the grain, but no differences in the ratio between total N incorporated into CP and total N occurred. The lack of effect of elevated CO_2, or supply of supplemental N, on incorporation of total C, and the "dilution" in concentration of total N in response to elevated concentrations of CO_2 in crops that did not receive high levels of N fertiliser on the C:N ratio of grain was similar to that for straw. The C:N ratio of grain harvested from crops supplied with low levels of N fertiliser, but grown in different concentrations of CO_2, were 22.0:1 and 19.9:1 for ambient CO_2 and FACE treatments, respectively. However if the crop was supplemented with N and grown under two different CO_2 regimes, a difference (P<0.05) in C:N ratio occurred (17.5:1 *versus* 14.4:1 for ambient and FACE treatments, respectively).

The effect of elevated concentrations of CO_2 and supply of N on non-structural carbohydrate (*i.e.*, WSC and starch) contrasted with the observations for straw harvested from the same treatments. Grain harvested from crops grown under elevated supply of CO_2 had higher concentrations of both WSC and starch (P<0.05). The concentration of starch in the grain that was grown with a higher supply of N from fertiliser occurred under FACE conditions increased by 13 g/kg DM. No difference in concentration of WSC occurred for crops gown under elevated CO_2 but for crops grown under conditions of ambient CO_2 the decrease was 8 g/kg DM (P<0.05). No effect of changing concentrations of CO_2 occurred for

ADF_{om}, lignin (sa), cellulose and NDCD, but concentration of hemicellulose was higher ($P<0.05$) in grain grown under ambient concentrations of CO_2 irrespective of supply of N to the crop. A weak interaction of CO_2 and N occurred for $aNDF_{om}$ concentration. Increasing the supply of N fertiliser did not alter concentrations of hemicellulose, ADF_{om} and digestibility of NDF (NDCD). Furthermore increased fertilisation increased the concentration of lignin (sa) ($P<0.01$) irrespective of supply of CO_2. No effect of increasing the concentration of CO_2 or supply of N to the crop occurred for total ash.

The responses of the grain to changes in CO_2 and supply of N to the crop had an impact on the gross energy of the grain, and the supply of N to the crop grown under both ambient and enriched CO_2 conditions reflected the increase in concentration of CP ($P<0.001$). At low levels of supply of N, there was a substantial decline in the CP to energy ratio (0.62 *versus* 0.45) in grain harvested from crops grown under enriched concentrations of CO_2 but these differences did not occur if the crop had received high levels of fertiliser N.

4. Discussion

The interaction between the supply of CO_2 and supply of N to wheat crops grown under water-fed (*i.e.*, no deficit) cropping are relatively well understood (Akin et al., 1995a,b; Pinter et al., 2000; Sinclair et al., 2000; Asseng et al., 2004). However, there is little information on impacts of these treatments on straw and grain quality for feeding to livestock, especially for feeds produced and used in developing countries where agronomic inputs may be limited.

4.1. Impact of elevated CO_2 and nitrogen supply on straw quality

Total C accumulation in straw was not affected by increasing the concentration of CO_2 by 200 μl/l, reflecting the previous study of Idso and Idso (2001). A decrease in $aNDF_{om}$, hemicellulose and lignin (sa) that did not seem to impact on the total C content. These changes may have implications on plant biomechanical characteristics and the overall quality of straw for ruminant feeding. Under conditions of increasing supply N at ambient CO_2 concentration, no increases in digestibility occurred suggesting no improvements in degradation of the straw in the rumen and no change in the requirement for supplementary N for microbial utilisation of this crop residue.

The impact of increasing CO_2 concentration, by approximately 200 μl/l above ambient, on accumulation of N in straw is important for ruminant feeding systems in areas where agronomic inputs (*i.e.*, fertiliser) may be limited, but animal production is extensive. The decline in concentration of N in the straw resulting from elevated CO_2 in systems receiving low levels of N is not a new observation (Bazzaz, 1990; Hocking and Meyer, 1991; Cotrufo et al., 1998). However, when considering the reduction in relation to animal production the “dilution” by increased accumulation of C and increased yield may not offset the reduction in supply of CP (an important limiting factor in animal production in many arid areas) when a complete production system is examined. It has been suggested that elevated CO_2 supply enhances production of total non-structural carbohydrate reflecting reductions in Calvin cycle enzymes and possibly reduced translocation of nitrate in response to a reduction in transpiration (Besford et al., 1990; Roumet et al., 1996; Conroy and Hocking, 1993). The mean reduction in concentration of total N with low N and high N inputs were 29.2% and 11.5% (overall mean reduction of 17.1%; a similar observation to Cotrufo et al. (1998) who estimated the reduction in nitrogen concentration because of growing the crop under elevated CO_2 of 14%). Furthermore, results reported in our study were not affected by water supply in this study. Akin et al. (1995a,b) reported that the digestibility of wheat straw was not affected by the interaction between enrichment of CO_2 and water stress, but there was a lack of consistency in the response between plant components and harvest date. Akin et al. did not, however, take the crop to full maturity (*i.e.*, harvest the crop at grain maturity and for straw) but examined the wheat crop for forage production or grazing.

The increase in the C:N ratio of straw could have profound implications on microbial degradation of that fraction and crop residues after incorporation into the soil. To date, there have been a limited number of studies on decomposition of straw and crop residues derived from plants grown under conditions of elevated CO_2, and results of these studies are not consistent and may reflect artefacts of conducting the studies under laboratory conditions (Couteaux et al., 1991; Cotrufo et al., 1994; Cotrufo and Ineson, 1996). However all studies suggest that changes in chemical composition of the plant, rather than changes in the soil microflora, are the most important factors affecting rate of decomposition (Swift et al., 1979; Melillio et al., 1982; Taylor et al., 1989; Kemp et al., 1994). The data reported here provides some evidence that the impact of elevated CO_2 on structural components of the crop (for instance cell wall content ($aNDF_{om}$), lignin (sa) and hemicellulose) is limited, which may reflect increased production of secondary plant compounds (Idso and Idso, 2001). Increases in secondary plant compounds (*e.g.*, phenylpropanoid compounds) have been suggested to reduce the digestibility of the cell wall (Hartley and Ford, 1989), but the change in concentration of these components in the lignin (sa) or hemicellulose fraction were small and did not alter the microbial digestion of the straw (Ball, 1992).

4.2. *Impact of elevated CO_2 and nitrogen supply on grain quality*

Grain yield and quality are affected by growth and development of the crop during vegetative growth (*i.e.*, pre-anthesis) and mobilisation of reserves during grain fill (Vouillot and Devienne-Barret, 1999). Enrichment of the atmosphere with CO_2 increases the number of grains per plant, but has little impact on harvest index (*i.e.*, ratio of grain to total plant biomass; Mulholland et al., 1998; Pinter et al., 1996). Increases in thousand grain weight with extra CO_2 have only been observed in treatments that received low levels of supplemental N (*i.e.*, 53.6 g/1000 grains with elevated CO_2 concentrations *versus* 51.3 g/1000 grains at ambient CO_2). During the pre-anthesis stage of growth, the final grain number is source (*i.e.*, leaf and stem reserves and efficiency of carbon assimilation) limited (Manderscheid et al., 2003). As post-anthesis grain fill is temperature, dependent and seems unaffected by changes in atmospheric CO_2 concentration (Mulholland et al., 1998), elevated CO_2 concentration primarily enhances grain number and not rate of grain fill. Grain N content was reduced by 26.4%, but only for plants grown under conditions of elevated CO_2 receiving relatively low levels of N fertiliser. This reduction is of a similar magnitude to observations by Manderscheid et al. (1995), Fangmeier et al. (1999) and Wu et al. (2004). This reduction may have important implications for animal production as reduced grain supply or low bushel weight grain especially when agronomic inputs are low.

The reasons for the reduction in grain N content and grain CP content reflect an increase in the concentration of storage polysaccharide (*i.e.*, starch) in the grain, and possibly a change in the partition of N compounds during growth and development of the crop, especially around anthesis (Conroy and Hocking, 1993; Cotrufo et al., 1998). In previous studies (for example Fangmeier et al., 1999) elevated atmospheric CO_2 caused small increases in starch content of grains from crops receiving low levels of N fertiliser. However, our results demonstrate that elevated CO_2 can increase in starch concentration in the grain of crops grown under either low or high N input (effect of enrichment by 200 μl/l of CO_2: 42 g/kg in low N treatment *versus* 40 g/kg in high N treatment). The reduction in N and CP content of grain reflect an interaction between elevated CO_2 and low N fertiliser inputs, and may have implications on protein quality (*i.e.*, digestibility and amino acid composition) for non-ruminant animals. Wu et al. (2004) recently reported that grain protein quality declined in response to elevated CO_2 due to a reduction in total CP content and, more importantly, lysine content of the protein. Even though their decline in lysine in response to CO_2 was only a trend (*i.e.*, $P<0.06$), the reduction in lysine still was 5.8% (Wu et al., 2004). The decline in protein:gross energy ratio (P:E ratio) in grain harvested from the FACE treatments receiving low levels of N fertiliser, compared to the ambient CO_2 treatments, may have important implications about the nutritional value of the grain. A reduction in the P:E ratio and lysine:energy ratio of feeds can reduce the incorporation of protein into the muscle of pigs (English et al., 1988).

In a study by Rogers et al. (1998) protein content of wheat grain declined under limited N conditions. This has important implications for developing countries where grain provides the main, or sole, source of energy and protein for much of the human population. Atmospheric temperature increases of between 2 and 4 °C may affect wheat grain composition even more than enrichment of atmospheric CO_2 (Tester et al., 1995; Williams et al., 1995; Morison and Lawlor, 1999). If future atmospheric changes involve increases in both temperature and CO_2, soil amendments with N fertiliser may be necessary to maintain grain protein concentrations.

5. Conclusions

Elevated concentrations of CO_2 caused grain and straw quality to be altered in a potentially adverse fashion. These changes may have implications for livestock production in systems that do not employ high levels of N fertilisation. However, elevated concentrations of atmospheric CO_2 were beneficial for development of above grain kernel weight as measured by thousand-grain weight. However grain quality, in terms of CP to energy ratio, can affected by increasing concentrations of CO_2 in the atmosphere and this may lead to a reduction in the supply of protein available to livestock production systems. To reduce the impact of CO_2 enrichment on grain quality, an increased supply of N fertiliser may be necessary, with concomitant negative impacts on soil and water quality.

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